

Environmental Aspects of Energy Production and Use

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Alternative Energy

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Main Ideas

- Multimedia impacts
 - Air pollution
 - Water pollution and ocean spills
 - Solid waste
- Impacts occur in extraction, refining, transportation, distribution and use
- Major impact is in air pollution
- Preliminary global warming discussion

The impacts that energy production and use have on the environment start with the extraction of the basic resource. The mining of coal and uranium and the drilling and extraction of oil and natural gas.

Some energy resources, such as coal or natural gas, have minimal refining. Crude oil undergoes extensive refining to produce a range of products that are used.

Both the initial fuel resource and refined products are transported by a variety of means. These include ships (for crude oil and petroleum products and some coal), rail (coal and some petroleum products), pipelines (crude oil, petroleum products, natural gas, and coal slurry), and trucks for local delivery of energy products to homes, commercial locations and retail gasoline distribution. Transportation has the possibility of accidental spills especially from tanker spills and pipeline ruptures.

Oil refinery processes also have a potential for accidents that can affect the environment, however the greatest potential for accidents comes from chemical plants that are preparing toxic compounds such as pesticides.

Electric power lines are another way of transporting energy from one point to another. This power transmission can remove the emissions associated with power production away from the point where the power is used. It can also remove the threat of accidents from nuclear power plants away from urban areas.

Much of these notes will examine air pollution which is the major environmental impact from energy production and use.

These notes will introduce the discussion of global warming, which will be continued next Tuesday.

Air Pollution

- Most of energy production and use is from fossil fuels
- Most air pollution comes from the combustion of fossil fuels
- Overall policy and deadlines governed by Federal Clean Air Act
- Regulations and enforcement a combination of federal, state and local efforts

Fossil fuels form the major link between energy resources and air pollution. Just as the majority of energy used in both the US and the world comes from fossil fuels, so too does the majority of air pollution.

The regulation of air pollution started in the 17th century when the King of England directed that certain smoky coals known as sea coals should not be burned in the City of London. Until the 1950s air pollution regulations were directed at the reduction of smoke and air pollution control was known as smoke prevention.

In the last century, there were two dramatic air pollution incidents in which air pollution led to increased mortality over a short time period. These occurred in the Muese Valley in Belgium in 1936 and in London in 1948. The main contaminants in these incidents were particulate matter and sulfur oxides. During the early 1940s air pollution started to appear in Southern California and experiments by Aarie Haagen-Smidt at Cal Tech during the 1950s showed that the main component of this pollution ozone which was formed in the atmosphere from reactions of hydrocarbons and oxides of nitrogen.

Although local and state efforts were made to control pollution and Federal Clean Air Act legislation was passed in 1955, 1963, and 1967, the first stringent Federal law as passed in the 1970 amendments to the clean air act. Amongst other provisions, these amendments directed the federal Environmental Protection Agency to issue criteria and standards for air pollutants that came from “numerous or diverse ... sources.” Such pollutants have become known as criteria pollutants.

Air pollution legislation and regulations deal separately with criteria pollutants and with toxic air contaminants.

Air Pollutants

- Criteria Pollutants
 - Come from “numerous or diverse mobile or stationary sources”
 - EPA administrator sets national ambient air quality standards (NAAQS)
 - Primary standards, “allowing an adequate margin of safety, are requisite to protect the public health”
 - Secondary standards to “protect the public welfare”

The EPA administrator sets two kinds of ambient standards: primary standards to protect public health and secondary standards to protect public welfare. The latter standards include such items as visibility, ecosystem damage, material damage, and agricultural crop losses.

States that exceed the NAAQS must prepare plans known as state implementation plans or SIPs to meet the standards. Primary standards must be met by a fixed deadline. There is no deadline for secondary standards.

Historically many areas of the country have been unable to meet the primary standards leading to revisions in the Clean Air Act in 1977 and 1990. Because of the problems in meeting primary standards there has been little emphasis on secondary standards.

One exception to this is the acid deposition program that was explicitly written into the Act with the 1990 amendments. This program is designed to reduce ecosystem damage caused by acidic gases that are deposited into lakes and other fragile ecosystems through rain or dry deposition. The main sources of acid deposition are from reactions in the atmosphere where sulfur and nitrogen oxides form sulfuric and nitric acid.

List of Criteria Pollutants

- Ozone (formed in atmosphere)
- Sulfur dioxide (primary pollutant)
- Nitrogen dioxide (direct and secondary)
- Particulate matter (direct and secondary)
- Carbon monoxide (direct)
- Lead (direct)

Ambient pollutants are either emitted directly from sources (so called primary pollutants) or formed by reactions in the atmosphere (so called secondary pollutants). Ozone is the main example of a secondary pollutant. It is formed by photochemical reactions between oxides of nitrogen and hydrocarbons typically called volatile organic compounds or VOCs.

Combustion sources emit two main oxides of nitrogen, nitric oxide, NO, and nitrogen dioxide, NO₂. The sum of these two compounds is written as NO_x (and pronounced nocks.) The majority of the NO_x emissions from combustion sources are NO. About 10% of the total NO_x emissions are NO₂. However, NO can react to form NO₂ in the atmosphere. NO is not considered hazardous to health directly, but NO₂ is. Presently there are no areas in the US that exceed the NAAQS for NO₂.

Sulfur dioxide, SO₂, emissions come almost exclusively from the combustion of sulfur containing fuels. (Sulfur processing plants are an additional source of SO₂.)

The regulation of particulate matter is based on size of the particles. This is defined in terms of the mean aerometric diameter, the diameter of a sphere with equivalent drag characteristics. The NAAQS for particulate matter have changed from a standard for total suspended particulate matter (which has a mean aerometric diameter of 30 μm.) to the current standard for particulate matter with a mean aerometric diameter of 2.5 μm. (From about 1980 to 2000 the standard was for particulate matter with a mean aerometric diameter of 10 μm.) The finer particles are better able to penetrate deeper into the lung and have a greater impact on human health for this reason. In addition, finer particles tend to be those that have a greater chemical toxicity. Thus control of fine particles is thought to provide greater health protection. Particulate matter is directly emitted and is formed in the atmosphere from reactions of gaseous precursors. The latter is called secondary particulate matter,

CO and lead originate mainly from gasoline-powered automobiles. The elimination of lead from gasoline has eliminated lead as a pollution problem in almost all areas.

Criteria Pollutant Control

- States prepare State Implementation Plans (SIPs) to achieve National Ambient Air Quality Standards (NAAQS)
- SIP requirements in Clean Air Act
- Attainment areas do not need SIPs
- Variety of requirements: NSR, NSPS, RACT, RFG, I&M, etc.

Since the 1970 amendments to the Act there have been several rounds of SIP submittals. SIPs that are prepared by states must be approved by EPA. To be approved the SIP must contain all the elements that Congress has required in the Act. In particular, it must show a plan of proposed regulations that will allow an area to meet the primary NAAQS by the required attainment date.

Among the various requirements are a preconstruction review and permit program for major new sources or major modifications to existing sources. This program is known as **New Source Review** or NSR. Permit programs are required in both attainment and nonattainment areas. In nonattainment areas the review must show that the new source will not degrade air quality. The nonattainment program is called PSD for **P**revention of **S**ignificant **D**eterioration. In attainment areas, NSR requires the user to use equipment that achieves the **L**owest **A**chievable **E**mission **R**ate (LAER) and obtain emission reductions for other sources that are greater than the emission increases caused by the new source. In attainment areas, sources are required to use **B**est **A**vailable **C**ontrol **T**echnology which is less stringent than LAER.

Since the 1970 amendments to the Act, EPA has been required to set **New Source Performance Standards**. These set minimum technology requirements for new sources.

In all SIPs states must include requirements that sources are retrofitted using **R**easonably **A**vailable **C**ontrol **T**echnology (RACT) as defined by EPA. Certain, more polluted, areas are required to use reformulated **g**asoline (RFG).

States must implement vehicle **I**nspection and **M**aintenance (I&M) programs. There are two program levels, basic and enhanced. Enhanced programs, which are required in more polluted areas, test the vehicle under load. Basic programs use an idle test.

Stationary sources also have an operating permit program that is required under Title V of the 1990 amendments to the Act.

Toxic Pollutants

- 1970 amendments to the act called on EPA to control “hazardous air pollutants”
- Only seven were regulated by 1990
- In 1990 amendments to the Act, Congress specified 189 pollutants, one of which was subsequently removed from the list

Reference: <http://www.epa.gov/ttn/atw/> (Accessed February 12, 2007)

In the 1970 amendments to the Act, hazardous or toxic pollutants were thought to be emissions that came from localized sources. This was in contrast to criteria pollutants that came from many and diverse sources. Thus hazardous pollutants were to be controlled under a separate regulatory scheme that did not make them part of SIPs or require NAAQS.

Another part of the reasoning for a separate control program was the idea that criteria pollutants have a threshold below which there are no health effects. Toxic pollutants, on the other hand, were considered to have no threshold. Thus toxic pollutants could not have a NAAQS that could be set with an adequate margin of safety. Recent research in standard setting has blurred the distinction between criteria pollutants and toxics in terms of health effects and the margin of safety.

The seven regulated toxic pollutants (under the program called NESHAPs for National Emission Standard for Hazardous Air Pollutants) were asbestos, benzene, beryllium, inorganic arsenic, mercury, radionuclides and vinyl chloride. The small number of regulated pollutants was due to the stringent requirements under the 1970 amendments for determining the risk of a hazardous pollutant prior to regulating it.

Noncancer risks are evaluated in terms of a reference concentration. This is an estimate (with uncertainty spanning perhaps an order of magnitude) of a continuous inhalation exposure to the human population (including sensitive subgroups which include children, asthmatics and the elderly) that is likely to be without an appreciable risk of deleterious effects during a lifetime. It can be derived from various types of human or animal data, with uncertainty factors generally applied to reflect limitations of the data used. (<http://www.epa.gov/ttn/atw/nata/gloss1.html#hazardquotient>)

Toxic Pollutant Control

- EPA to promulgate Maximum Achievable Control Technology (MACT)
- EPA to consider residual risk after application of MACT
- Use Generally Available Control Technology for area sources

EPA is required to establish Maximum Achievable Control Technology (MACT) standards for major sources that emit more than 10 tons per year of any listed HAP or 25 tons per year of a mixture of HAPs. For existing source categories, MACT standards must be at least as stringent as the degree of control achieved by the best-performing 12% of sources in source categories with more than 30 facilities, or by the best five sources in smaller source categories.

Standards may include operational improvements and implementation is done by individual states by permit requirements for the affected facilities.

Within eight years after a MACT standard is issued, EPA must assess the residual risk associated with the source category and issue additional standards adequate to provide an ample margin of safety to protect public health and, after considering costs and feasibility, the environment. EPA has begun residual risk assessments, but none have been completed.

EPA is also to set standards for area sources that require a lower level of controls. This level of control technology is known as GACT for generally available control technology.

Mobile sources have been found to be a major source of toxic emissions. These emissions include benzene, 1,3-butadiene, formaldehyde, acetaldehyde. EPA projects that future regulations to reduce VOCs from motor vehicles will reduce emissions of these toxic pollutants. Except for regulations to hold refineries to current levels of "overcompliance" with regulations for levels of toxic compounds in gasoline, EPA has proposed no further regulations on mobile source toxics.

List of Toxic Pollutants

- See notes for start of list
- Many compounds are listed here, but EPA is currently examining thirty compounds that contribute most of risk
- Toxic pollution was once associated with individual factories, but mobile sources produce a large amount of toxic pollutants

Acetaldehyde	Acetamide	Acetonitrile	Acetophenone	2-Acetylamino-fluorene
Acrolein	Acrylamide	Acrylic acid	Acrylonitrile	Allyl chloride
4-Aminobiphenyl from gasoline)	Aniline	o-Anisidine	Asbestos	Benzene (including benzene
Biphenyl	Benzidine	Benzotrichloride	Benzyl chloride	
Bromoform	Bis(2-ethylhexyl)phthalate (DEHP)	Calcium cyanamide	Bis(chloromethyl)ether	
Carbaryl	1,3-Butadiene	Carbon tetrachloride	<u>Caprolactam</u>	Captan
Catechol	Carbon disulfide	Chlordane	Chlorine	Carbonyl sulfide
2-Chloroacetophenone	Chloramben	Chlorobenzene	Chlorobenzilate	Chloroacetic acid
Chloromethyl methyl ether		Chloroprene	Cresols/Cresylic acid (isomers and mixture)	Chloroform
o-Cresol	m-Cresol	p-Cresol	Cumene	2,4-D, salts and esters
DDE	Diazomethane	Dibenzofurans	1,2-Dibromo-3-chloropropane	
Dibutylphthalate	1,4-Dichlorobenzene(p)		3,3-Dichlorobenzidene	
Dichloroethyl ether (Bis(2-chloroethyl)ether)			1,3-Dichloropropen	Dichlorvos
Diethanolamine	N,N-Diethyl aniline (N,N-Dimethylaniline)			Diethyl sulfate
3,3-Dimethoxybenzidine		Dimethyl aminoazobenzene		3,3--Dimethyl benzidine
Dimethyl carbamoyl chloride		Dimethyl formamide	1,1-Dimethyl hydrazine	
Dimethyl phthalate	Dimethyl sulfate	4,6-Dinitro-o-cresol, and salts		2,4-Dinitrophenol
2,4-Dinitrotoluene	1,4-Dioxane (1,4-Diethyleneoxide)		1,2-Diphenylhydrazine	
Epichlorohydrin (l-Chloro-2,3-epoxypropane)			1,2-Epoxybutane	
Ethyl acrylate	Ethyl benzene	Ethyl carbamate (Urethane)		Ethyl chloride (Chloroethane)
	Ethylene dibromide (Dibromoethane)		Ethylene dichloride (1,2-Dichloroethane)	
Ethylene glycol	Ethylene imine (Aziridine)		Ethylene oxide	Ethylene thiourea
Ethylidene dichloride (1,1-Dichloroethane)			Formaldehyde	Heptachlor
Hexachlorobenzene		Hexachlorobutadiene		
Hexachlorocyclopentadiene		Hexachloroethane	Hexamethylene-1,6-diisocyanate	
Hexamethylphosphoramide		Hexane	Hydrazine	Hydrochloric acid
Hydrogen fluoride (Hydrofluoric acid)		Hydrogen sulfide	Hydroquinone	Isophorone
Lindane (all isomers)		Maleic anhydride	Methanol	Methoxychlor
Methyl bromide (Bromomethane)		Methyl chloride (Chloromethane)		Methyl chloroform (1,1,1-
Trichloroethane)	Methyl ethyl ketone (2-Butanone)		Methyl hydrazine	Methyl iodide (Iodomethane)
	Methyl isobutyl ketone (Hexone)		Methyl isocyanate	Methyl methacrylate

Air Pollution Sources

- Stationary sources
 - Point – large individual sources like power plants with specific emission locations
 - Area – distributed sources like gasoline stations or dry cleaners
- Mobile sources
 - Onroad – cars, trucks, buses, motorcycles
 - Offroad – agriculture and construction equipment, lawn and garden equipment, locomotives, aircraft, forklift trucks, boats, recreational vehicles, offroad motorcycles.

Source classifications are used both for control regulations and for determination of source emissions. The process of determining emissions from all sources is known as obtaining an emissions inventory. This process has large uncertainties and is based on the use of emission factors.

Regulations for stationary sources are usually set by state or local agencies. EPA has to approve regulations that are part of SIPs and may not approve regulations that are not stringent enough.

Mobile source regulations are done mainly by EPA. California is the only state that has the authority to set separate exhaust standards for mobile sources. States can regulate the fuel that is used by mobile sources and states are responsible for maintaining vehicle inspection and maintenance programs.

Emission controls for cars started in the 1960s with regulations that required crankcase ventilation gases to be recirculated back into the engine. Exhaust emission limitations started in California in 1966 and nationally in 1968. Controls on evaporation of fuel vapors from vehicles started in 1970.

Regulation of truck emissions started in the late 1970s and emission limitations on offroad sources started in 1990.

The sequence of regulation was based on the idea of starting on the largest problems first. As a result of the stringent control regulations, now and in the future, for cars and trucks, offroad sources are predicted to contribute an increasing amount to emissions.

Emission Inventories

- Product of emission factors and activity
 - $\text{mass/time} = \text{mass/product} * \text{product/time}$
- Subject to large uncertainty in both emission factors and activity data
- Large point sources have continuous emission monitors
- Other sources have single source tests or use average factors from other data

The calculation of emission inventories is central to good air quality planning, regulation, and enforcement. Unfortunately, the calculation of inventories is fraught with uncertainties.

There are very few cases in which emissions are directly measured. Direct measurements are only required on large emission sources that use continuous emission monitors to obtain the mass emission rate of pollutants. In other cases emissions are estimated by emission factors that relate emissions to activity data that are more typically monitored.

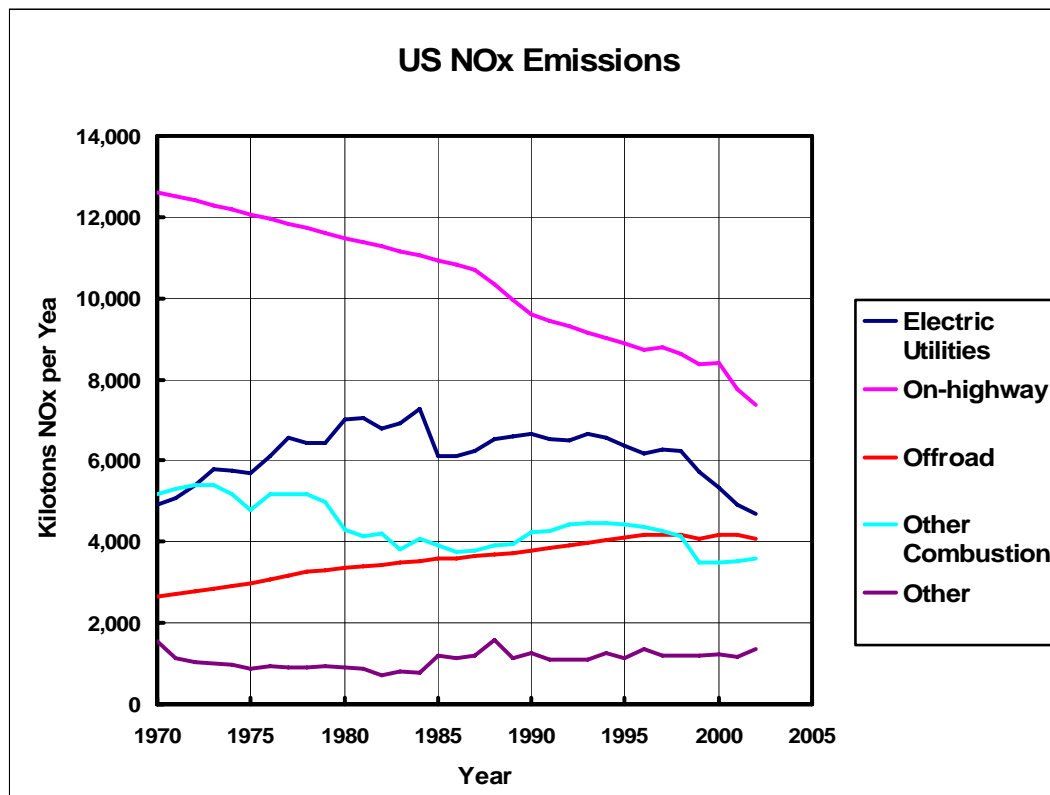
In combustion processes, many emission factors are linked to the heat input rate for the process. Since fuel flow rates are usually measured and the heating value of the fuel is reasonably well known, this provides an estimate of the emissions.

Obtaining emissions for all sources in a region, particularly a large urban region, can be a data collection nightmare, with the need to obtain data from a large number of sources.

Accurate emission factors account for the operating conditions since emissions factors for many processes can change with load.

As discussed below the link between emissions and ambient concentrations is based on air quality models. Such models require the knowledge of how emissions vary over space and time in a particular region. Obtaining this information increases the requirements for inventory collection.

Mobile source emission inventories are a particular problem. These inventories (using programs such as EPA's MOBILE6 or California's EMFAC 2000) are based on measurements of a sample of operating vehicles. However, research has found that a large proportion of vehicle emissions comes from a small percentage of the population that are high emitters. Obtaining a good measure of the distribution of vehicles as normal or high emitters has proven difficult.



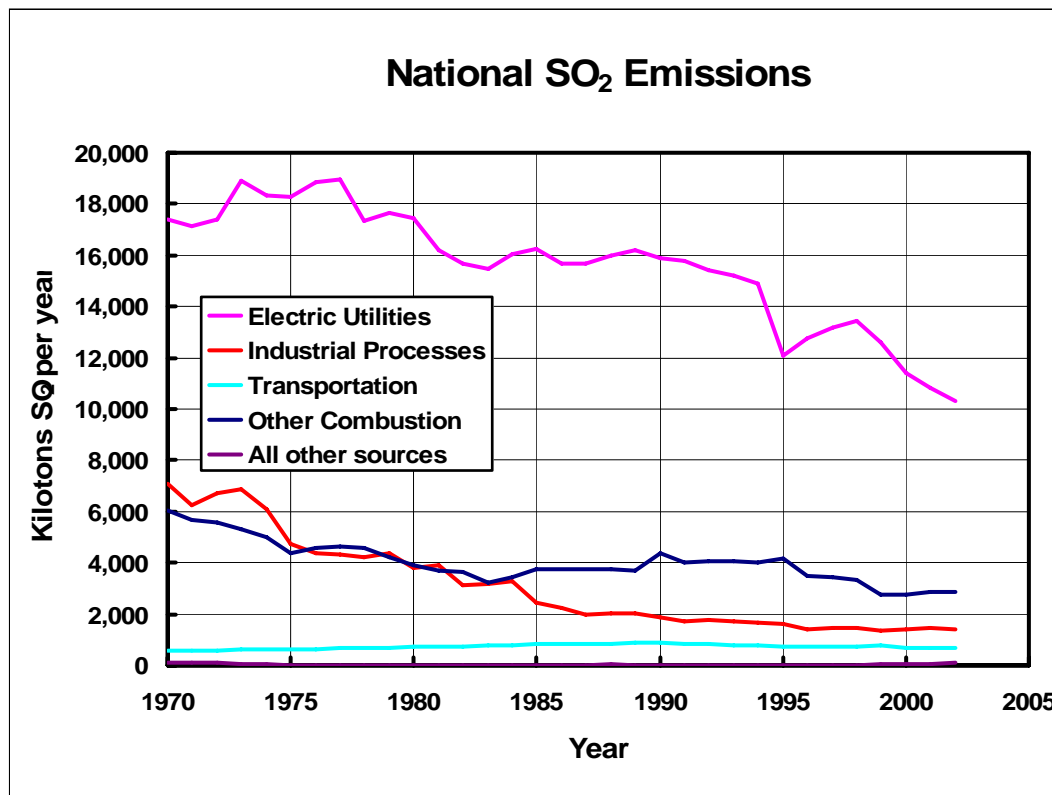
NO_x is a pollutant that comes from mainly from combustion. Both mobile and stationary sources play a role in NO_x emissions.

Control programs in place at the enactment of the 1970 amendments to the Clean Air Act and subsequent control programs have reduced NO_x emissions from cars and trucks on highway. However, emission reductions in other source categories have come much later in time. Nonroad NO_x emissions are a growing source. In 1970 they were regarded as a small source, but their control has been in effect since the late 1990s.

Reference: <http://www.epa.gov/ttn/chief/trends/index.html#tables> (Accessed February 11, 2007)

The data are provided in a series of Excel spreadsheet files that are grouped into a single zip file that was downloaded from this site.

Obscure fact: Although the majority of NO_x emissions are NO rather than NO₂, the reported NO_x emissions use the molar mass of NO₂ to convert all molar measurements of NO + NO₂ to reported mass inventory data for NO_x.



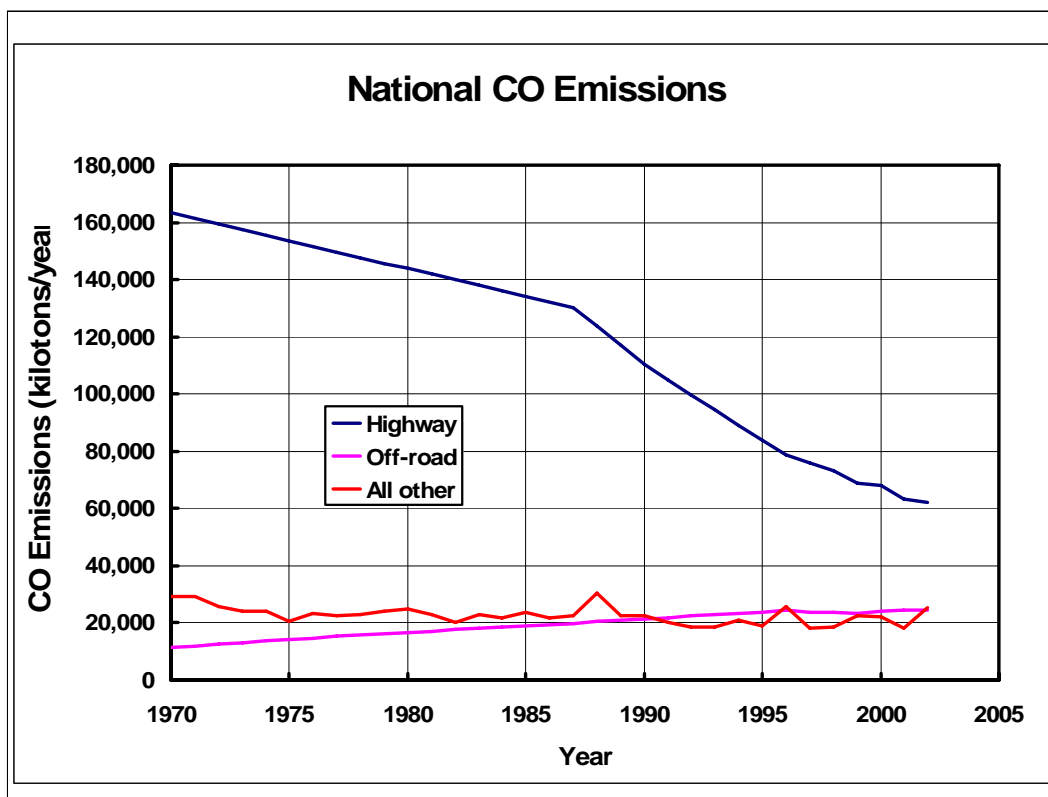
SO₂ is a pollutant that comes overwhelmingly from stationary sources. Combustion of sulfur containing fuels, coal in particular, accounts for most of the emissions of SO₂. Other sulfur oxides that are formed in the combustion process typically recombine with water formed during combustion and become part of particulate matter.

Reductions in SO₂ after 1990 are due to the acid rain provisions of the 1990 amendments to the Clean Air Act. The bump between 1995 and 1999 was due to the form of the acid rain provisions that rewarded early reductions in the Phase I period by allowing companies who had early emissions to defer compliance with the more stringent Phase II emission limits.

Transportation sources make a small contribution to SO₂ emissions because the sulfur content of vehicle fuels was initially limited by requirements for engine performance and refinery requirements for use of catalysts in oil refining. Subsequent regulations for motor vehicles fuels have limited sulfur even more, but there have been increased emissions due to greater use of diesel fuels. Currently enacted regulations that take effect between 2006 and 2012 will reduce this already small contribution to SO₂ emissions.

Reference: <http://www.epa.gov/ttn/chief/trends/index.html#tables> (Accessed February 11, 2007)

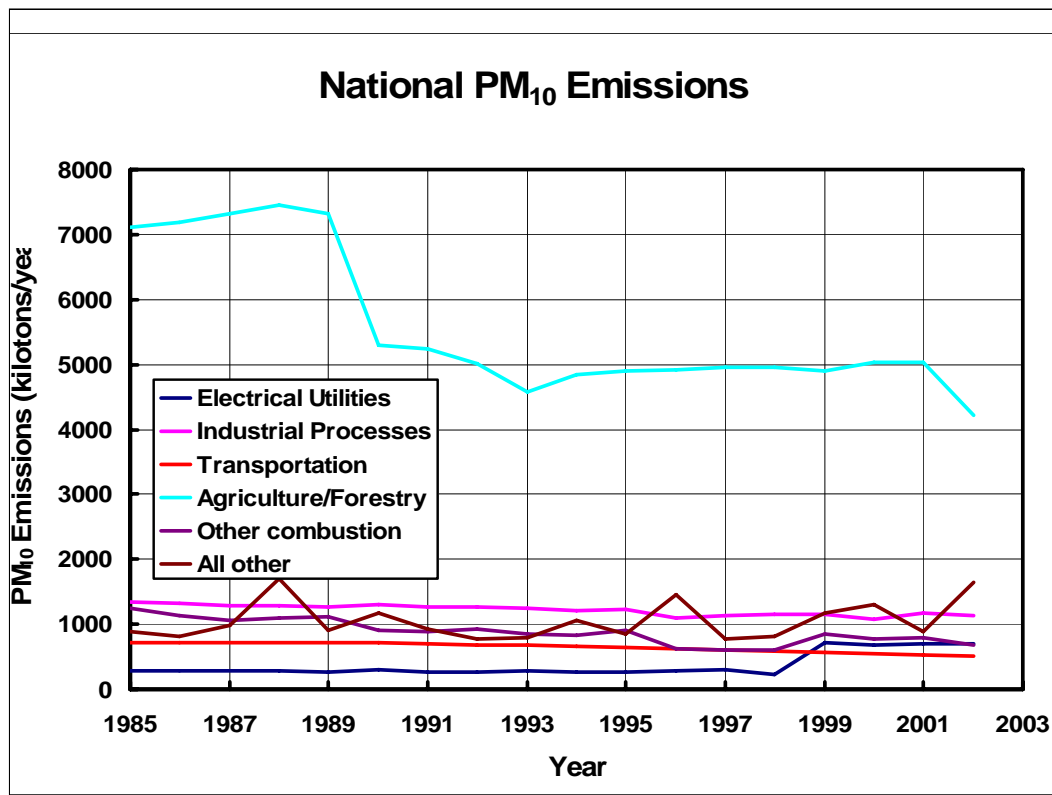
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CO is overwhelmingly a pollutant that comes from mobile sources, particularly gasoline-powered engines. Control programs to reduce this pollutant by catalytic converters have been successful over the past few decades.

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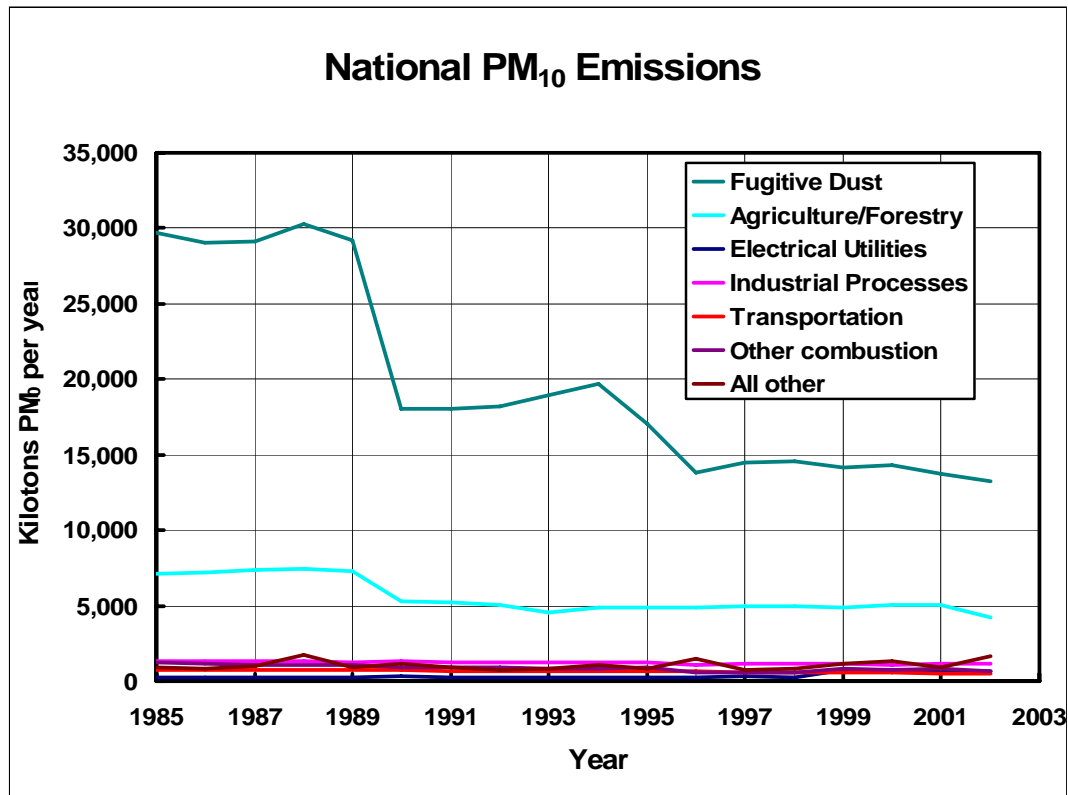
Particulate matter has been considered a criteria pollutant from the start of the consideration of criteria pollutants, but the diameter of the particulate considered has changed. Initial criteria considered total suspended particulates (TSP) that had a diameter less than 30 micrometers. Subsequent considerations of health effects led to a consideration of PM₁₀ shown here. Current criteria consider both PM₁₀ and PM_{2.5}.

PM₁₀ comes mainly from agriculture and forestry; this is mainly dust from agricultural operations. Industrial processes make the second largest contribution, mostly from materials processing.

Although combustion sources make a smaller contribution to this source category than they do to other categories, the particulate matter from combustion sources have a chemical nature that is more hazardous to human health than other particulate matter. Diesel particulate matter has been classified as a toxic air contaminant by the California Air Resources Board. The US EPA believes that the data on diesel particulate matter do not allow a full risk assessment and they track diesel particulate matter as a separate category when they consider toxic emission inventories.

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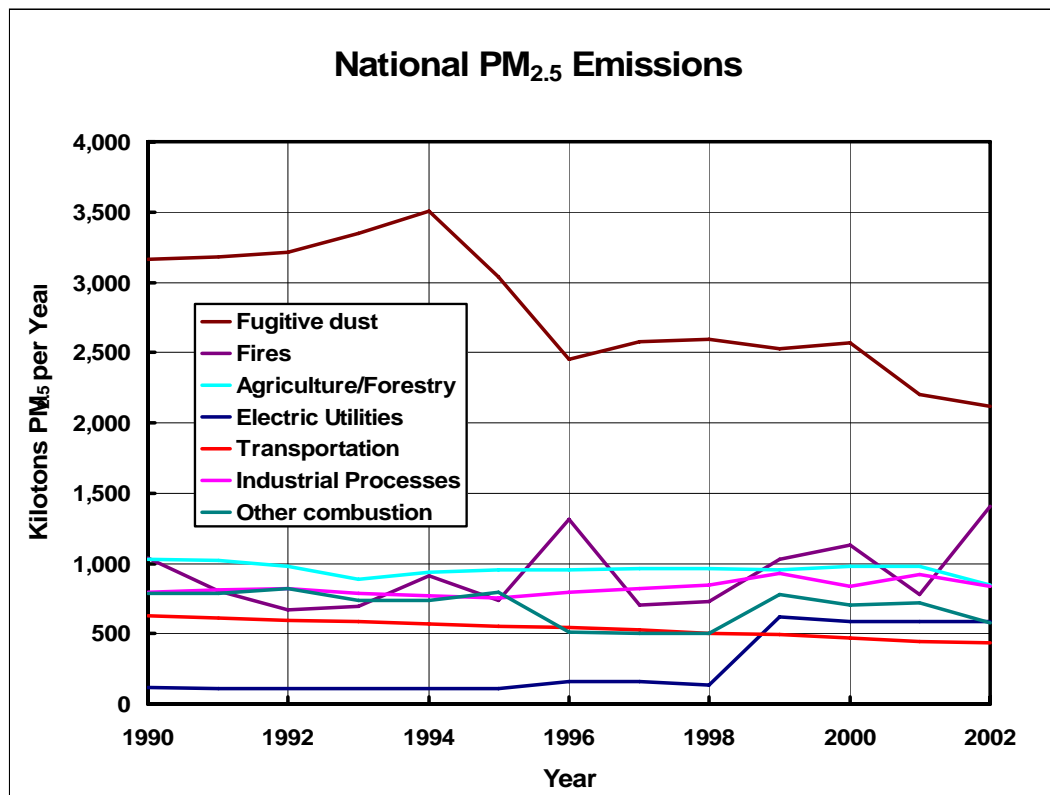


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PM₁₀ comes mainly from fugitive dust and agriculture and forestry; this is mainly dust from unpaved roads and agricultural operations. Industrial processes make the second largest contribution, mostly from materials processing.

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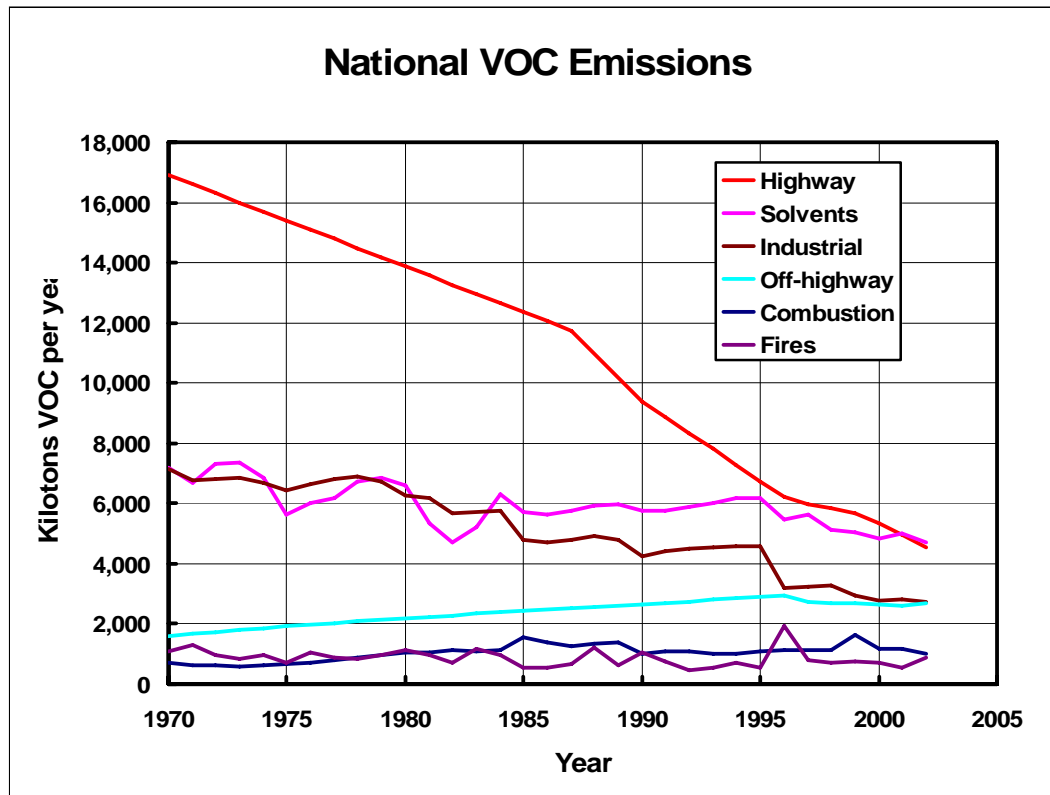


PM_{2.5} like PM₁₀ comes mainly from fugitive dust and agriculture and forestry; this is mainly dust from agricultural operations. However, combustion processes make a relatively larger percent contribution to PM_{2.5} than they do to PM₁₀. This is because most combustion particulate is very small diameter.

Although combustion sources make a smaller contribution to this source category than they do to other categories, the particulate matter from combustion sources have a chemical nature that is more hazardous to human health than other particulate matter. Diesel particulate matter has been classified as a toxic air contaminant by the California Air Resources Board. The US EPA believes that the data on diesel particulate matter do not allow a full risk assessment and they track diesel particulate matter as a separate category when they consider toxic emission inventories.

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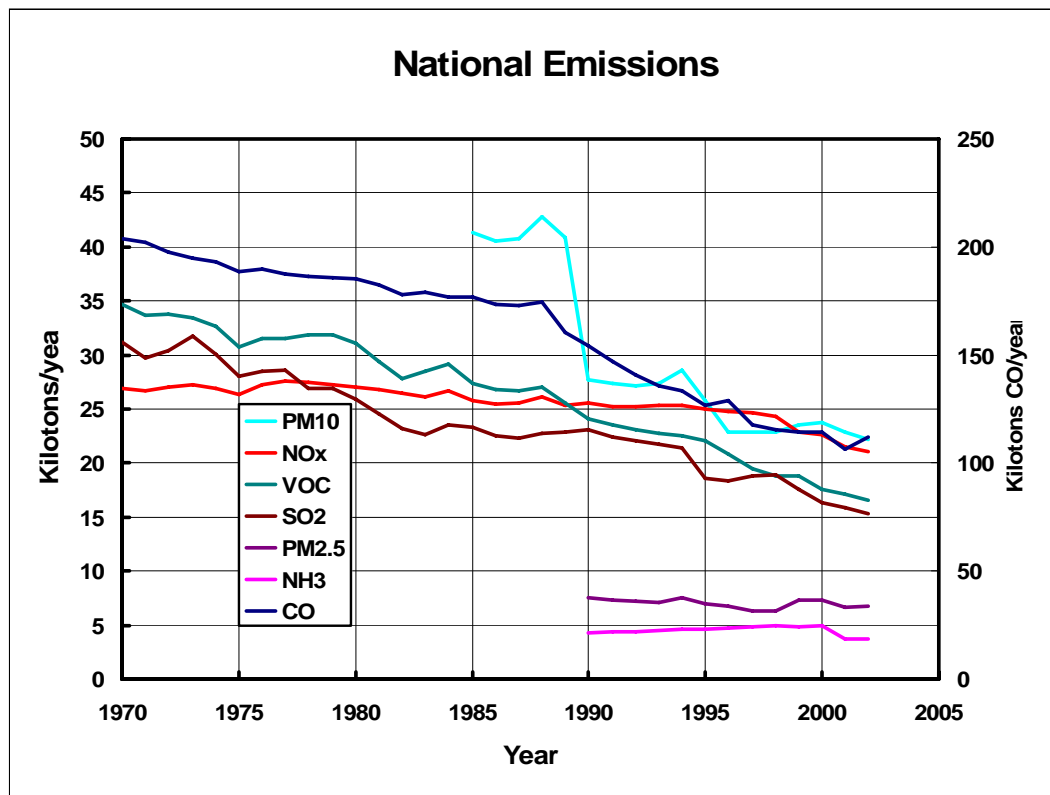
VOC is an acronym for volatile organic compounds. This refers to hydrocarbons that are active in the formation of ozone. Methane is not considered a VOC since it does not participate in ozone formation.

The major source of VOC emissions, highway vehicles, has been under increasingly stringent controls since the 1960s as shown. Off-road vehicles have continued to grow however.

Emissions from combustion processes are low because most combustion processes operate so as to minimize these emissions of unburned fuel. Electric utility emissions are only a small fraction of the total because the large sizes of electric power boilers make the combustion process particularly efficient.

Reference: <http://www.epa.gov/ttn/chief/trends/index.html#tables> (Accessed February 11, 2007)

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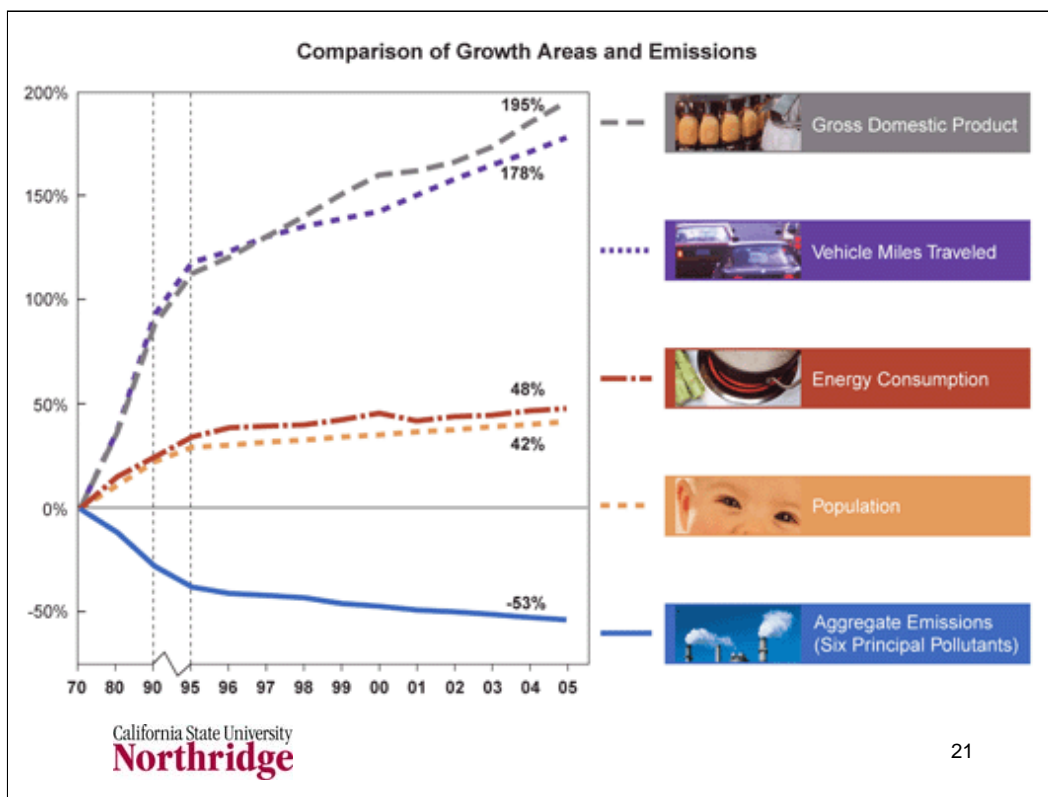
National statistics are misleading. In some urban areas, like Los Angeles, significant reductions in emissions have occurred. However, in other areas emissions have increased. Thus the national emission trends appear to show only a slight decrease, but the ambient air quality has improved in areas where it was particularly bad.

The graph above shows emissions for ammonia which is not regarded as a pollutant in its own right. However, ammonia can contribute to the formation of ammonium nitrate and ammonium sulfate what become particular matter. Although this role for ammonia has been known for several years, the potential need to control ammonia emissions has only been recently considered. Thus the inventory for this species starts in 1990.

Lead emissions are not shown here because lead emissions have been virtually eliminated as an air pollutant due to its removal from gasoline.

Reference: <http://www.epa.gov/ttn/chief/trends/index.html#tables> (Accessed February 11, 2007)

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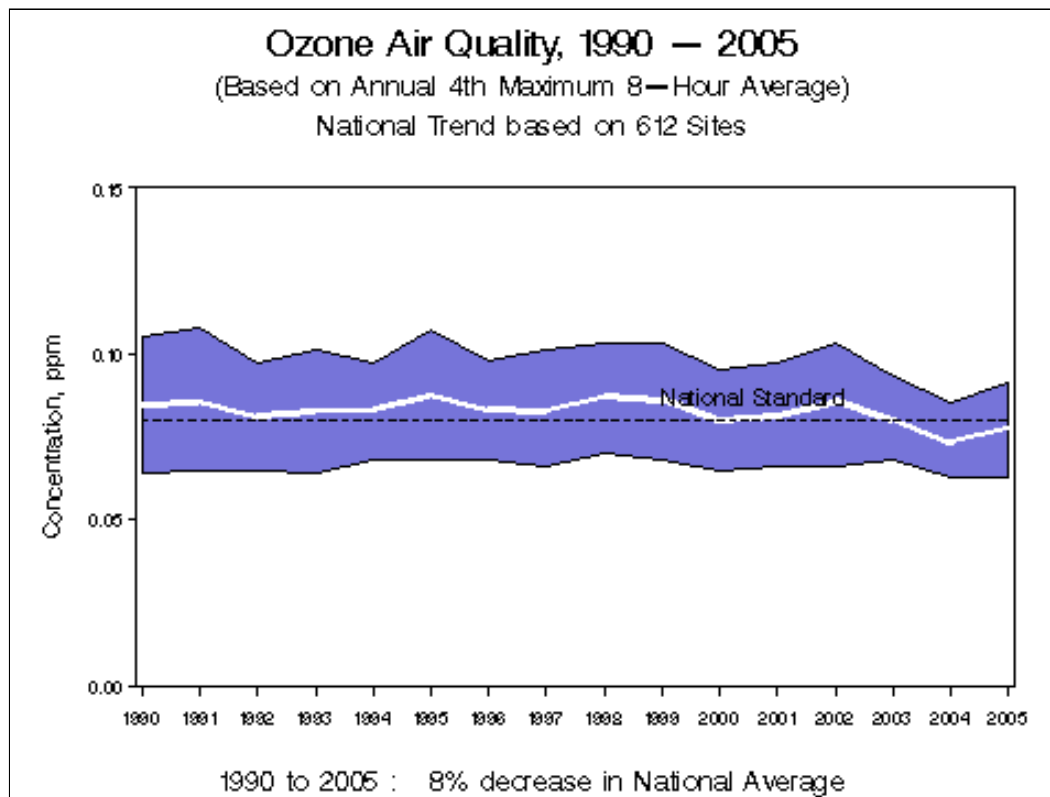


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Reference: <http://www.epa.gov/airtrends/econ-emissions.html> (accessed February 8, 2007)

The increased level of personal and economic activity shown here would be expected to increase emissions. The vehicle miles traveled (VMT) data indicate that in the absence of a motor vehicle control program, emissions from motor vehicles would have increased by 170% in the absence of a control program.

The most significant reduction has been in lead which has been virtually eliminated as an air pollutant due to its removal from gasoline.



Reference: <http://www.epa.gov/airtrends/ozone.html> (accessed February 8, 2007)

The following information is provided on interpreting the graph.

The blue band shows the distribution of air pollution levels among the trend sites, displaying the middle 80 percent. The white line represent the average among all the trend sites. Ninety percent of sites have concentrations below the top line, while ten percent of sites have concentrations below the bottom line.

For the Ozone (8-hour) standard used for comparison here the concentration plotted is the annual 4th maximum 8-hour average.

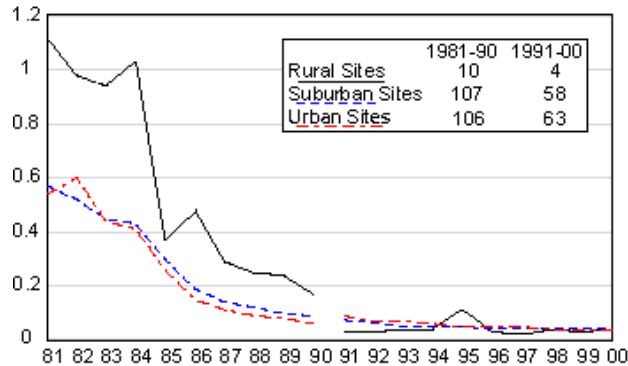
Ozone has been one of the most intractable air pollution problems. Despite efforts in the reduction of its precursors, VOC and NO_x, it continues to have high levels throughout the US.

Ambient Lead Levels

Figure 2-9. Pb maximum quarterly mean concentration trends by location (excluding point-source oriented sites), 1981-2000.

Pb Trend by Location, 1981-2000

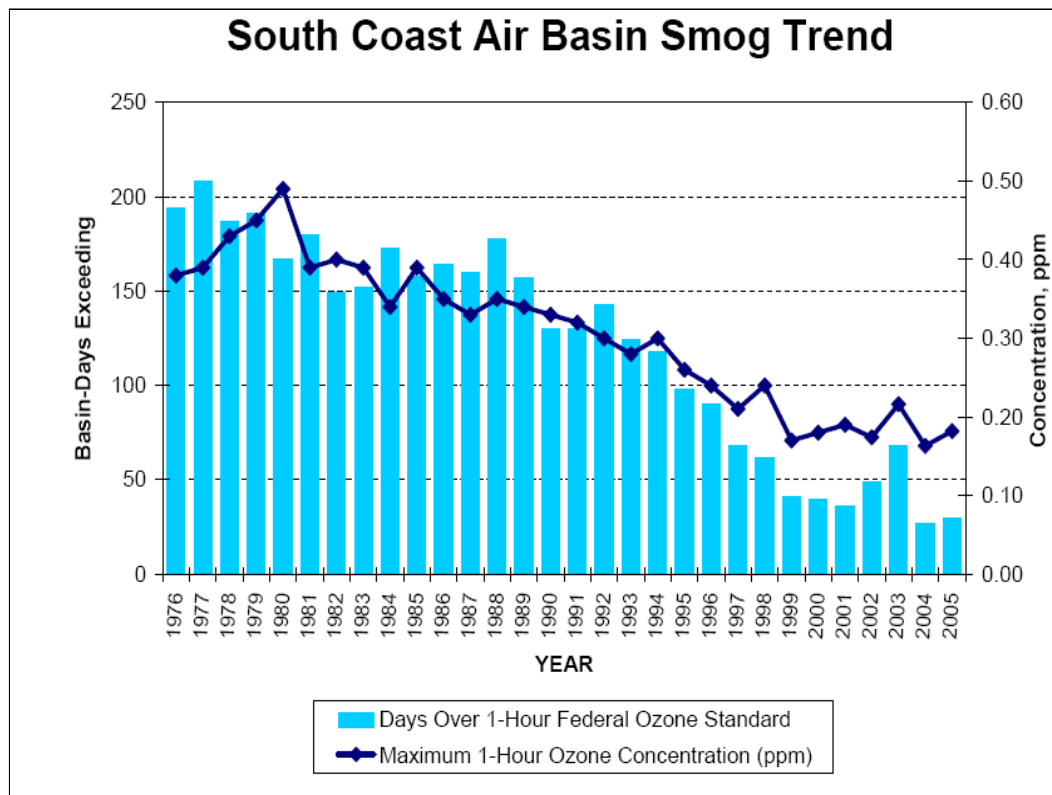
Concentration, $\mu\text{g}/\text{m}^3$



California State University
Northridge

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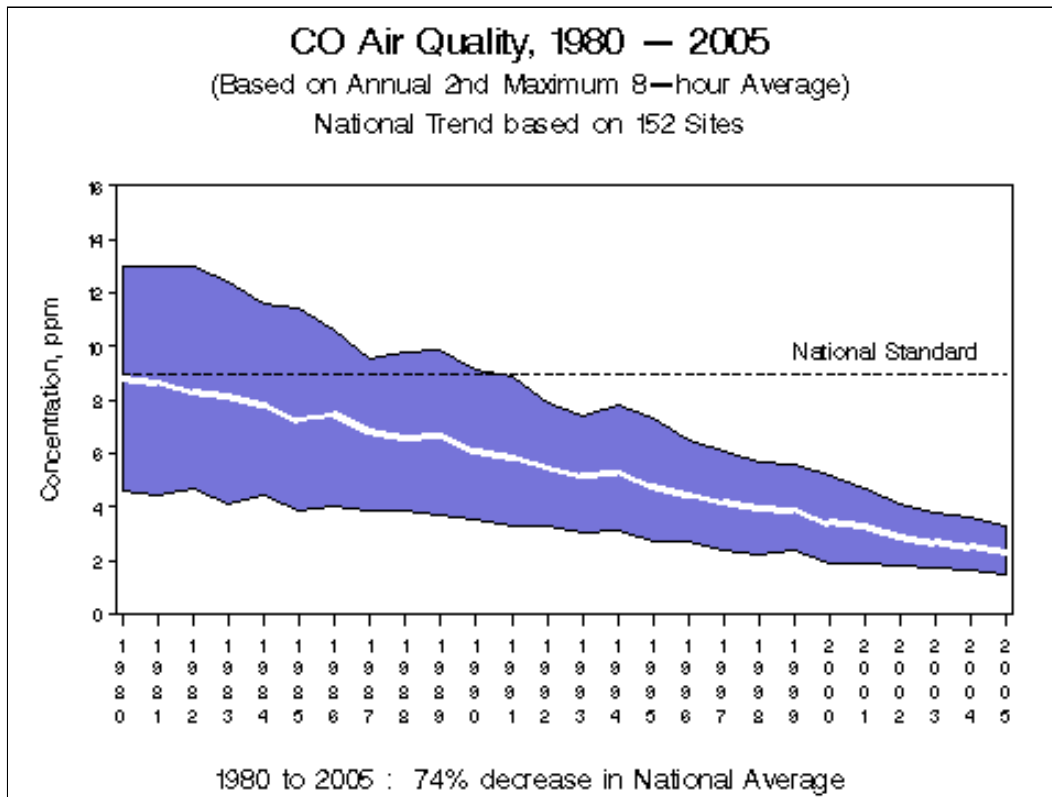
The greatest success in air pollution control has been the reduction in lead emissions and the resulting lead concentrations in the atmosphere. Almost all of this reduction has come from the removal of lead from gasoline. At present, most lead emissions come from facilities that process lead or use it. Battery plants are a common source of lead emissions in many urban areas. You will sometimes see Proposition 65 warnings from lead plants in newspapers. Based on a negotiated settlement of a lawsuit, these warnings show a map of the likely high concentration regions around the plants.



Reference: <http://www.aqmd.gov/> (accessed February 8, 2007)

Ozone levels in the South Coast Air Basin (SCAB) the region that includes most of Los Angeles County (as well as Orange County and portions of Riverside and San Bernardino counties) has shown a significant ozone reduction over the period of pollution abatement. (The Los Angeles County Air Pollution Control District, the precursor to the South Coast Air Quality Management District (SCAQMD), was founded in 1947.

The federal standard for ozone is 0.12 ppm for a one-hour average. The standard is not to be exceeded more than once in three years.



Reference: <http://www.epa.gov/airtrends/carbon.html> (accessed February 8, 2007)

The downward trend in CO concentrations mirrors the downward trend in CO emissions. This is to be expected for a pollutant that is not involved in atmospheric reactions.

Air Quality Models

- Link between emissions and ambient
- Simplest: ambient proportional to emissions
- Most complex: detailed numerical solution of three-dimensional equations
 - Meteorology
 - Chemical kinetics with multiple phases

SIPs are planning documents that require a model which links the effects of emissions reductions to reductions in ambient concentrations. The simplest of these is a proportional model, called linear rollback. This model works reasonably well for pollutants which are directly emitted and are not formed by reactions in the atmosphere. CO is a good example of this. In this model the emissions, E , are proportional to the difference between the actual concentration, C , and the background concentration, C_b .

$$E = k(C - C_b)$$

If the present emissions and concentration are represented as E_p and C_p , respectively, and the future emissions and concentration are represented as E_f and C_f , the emissions reduction, $(E_p - E_f)/E_p = 1 - E_f/E_p$ is given by the following equation.

$$1 - E_f/E_p = 1 - [k(C_f - C_b)] / [k(C_p - C_b)] = \{ (C_p - C_b) - (C_f - C_b) \} / (C_p - C_b)$$

Thus, under linear rollback, the required emission reduction is found from the following equation

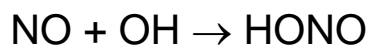
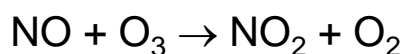
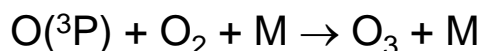
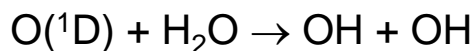
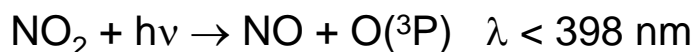
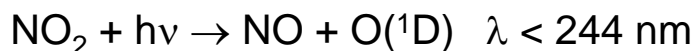
$$\text{Reduction} = 1 - E_f/E_p = (C_p - C_f) / (C_p - C_b)$$

This is a simple relationship between emissions and ambient concentrations. Unfortunately, it does not hold for pollutants that are formed by reactions in the atmosphere.

In addition to planning models that cover an entire urban area, there are point source models that are used to determine the impact of single sources on the areas around the source. Such models are used in decisions about construction permits for new sources or major source modifications.

Atmospheric Photochemistry

- Basic mechanism known since 1950s



Photochemical reactions (chemical reactions in the presence of sunlight) produce photochemical smog. The criteria pollutant associated with photochemical smog is ozone. Ozone is produced by a complex series of reactions a small number of which are shown on this and the next slide.

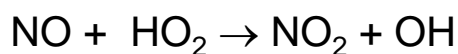
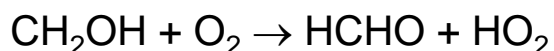
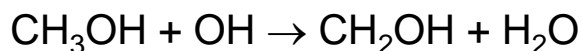
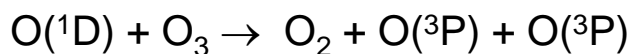
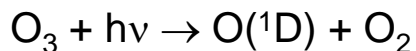
The reaction steps on the chart are the reactions that are regarded as the start of the mechanism for photochemical smog formation. In these reactions the symbol $h\nu$ represents the photochemical energy that splits a molecule. Such a reaction is known as photolysis. The (${}^1\text{D}$) and (${}^3\text{P}$) indicate the electronic energy states of the oxygen atoms that are formed in the reactions. Recall that the visible part of the spectrum lies between 300 and 700 nm and shorter wavelengths mean higher frequencies that correspond to greater energy in the photon participating in the reaction.

The symbol M represents a collision partner, sometimes called a third body. This means that another molecule must participate in the reaction to absorb energy. The presence of this third body affects the form of the equation used to model the rate of the reaction.

Compounds like O atoms, hydroxyl (OH), and HONO are called free radicals. These are highly reactive atoms or molecules that have an unbound electron. They are not ions because they have the same number of protons and electrons, but the bonding structure of the radicals makes them want to enter into reactions with other molecules.

Atmospheric Photochemistry 2

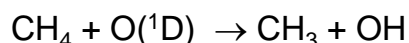
- Other reactions



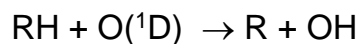
Additional reactions are shown in this slide. This reaction shows the participation of additional free radical reactions and additional photolysis reactions.

These reactions show how intermediate products such as formaldehyde (HCHO) and nitric acid (HNO₃) can be produced.

There is a general set of hydrocarbon reactions that have not been shown here. One such reaction is shown below.

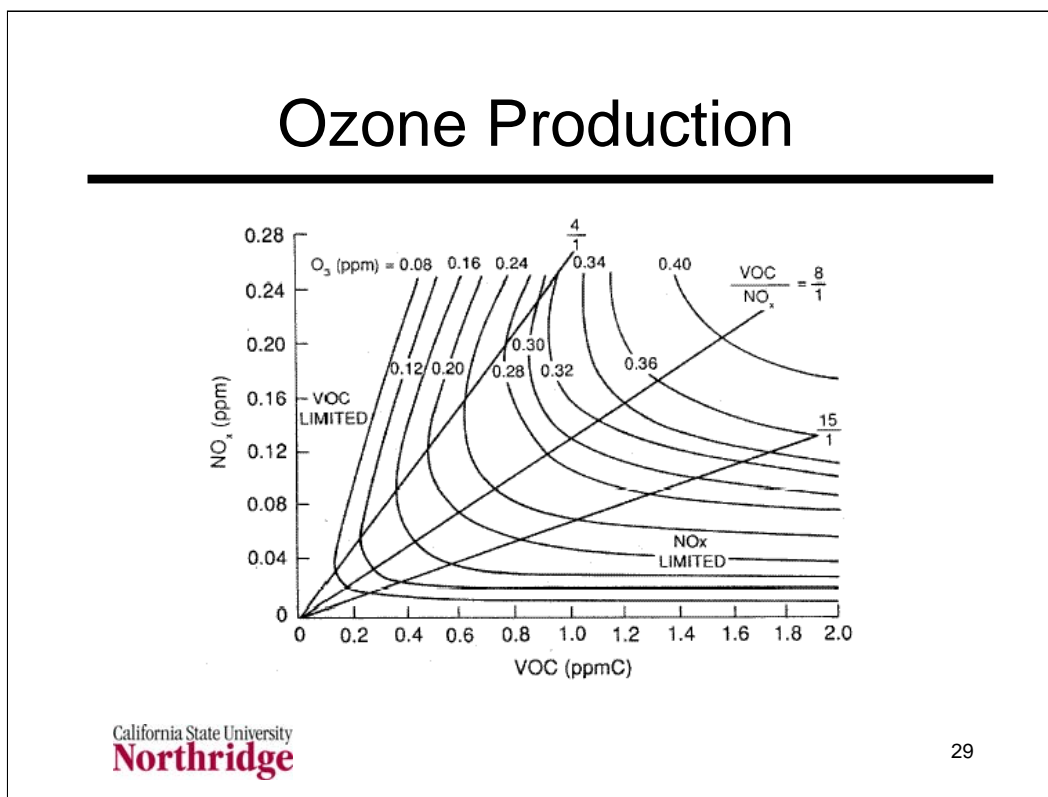


This is called a chain branching reaction because there is one free radical in the reactants and two free radicals in the products. Other hydrocarbons can participate in similar reactions. The general reaction equivalent to the one shown above for methane, may be written as follows.



In this general reaction, R represents some radical containing hydrogen and carbon atoms. For example, in the methane reaction R = CH₃.

The wide range of reactions that can take place lead to different amounts of ozone. Detailed chemical kinetic models are required to simulate the entire mechanism.



The diagram shown here, called an EKMA diagram, is taken from National Academy of Sciences, *Rethinking the Ozone Problem*, 1991, which says that the diagram was adapted from a 1977 reference to Dodge. (EKMA stands for **E**mpirical chemical **K**inetics **M**odeling **A**pproach.) This diagram formed the basis for air quality planning in the late 1970s and early 1980s. The basic point of this diagram – the need to choose controls over hydrocarbons or NO_x as a way to control ozone – remains true today even when more sophisticated models are used.

This diagram was based on experimental data which showed that the amount of ozone formed in photochemical smog depended on the initial concentration of reactants, volatile organic compounds (VOC) and oxides of nitrogen (NO_x). When the VOC/NO_x ratio is about 4/1 or less, the reaction is VOC limited. This region is on the left side of the diagram. Here ozone is reduced by controlling VOC. In this region, controls on NO_x will actually increase ozone.

When the ratio of VOC/NO_x is about 15/1 or more, as shown in the lower right side of the diagram, the control of NO_x is the best way to reduce ozone. Between these limits, reductions in either NO_x or VOC will reduce ozone.

The limitation of the EKMA model is that it gives a single value for an urban area. Recent models use the full integration of partial differential equations to examine photochemical reactions with variation of emissions and wind over space and time.

Attainment Classifications

- Ozone and CO nonattainment areas have various classifications
- Definitions are from 1990 amendments to the Act
- Different classifications lead to different attainment dates depending on area
- Also have different SIP requirements

Classification of Nonattainment Areas for Ozone and Carbon Monoxide

Ozone Nonattainment Areas		
Area classification	Design value	Attainment date*
Marginal	0.121 up to 0.138 ppm	November 15, 1993
Moderate	0.138 up to 0.160 ppm	November 15, 1996
Serious	0.160 up to 0.180 ppm	November 15, 1999
Severe–15**	0.180 up to 0.190 ppm	November 15, 2005
Severe–17**	0.190 up to 0.280 ppm	November 15, 2007
Extreme	0.280 ppm and above	November 15, 2010

Carbon Monoxide Nonattainment Areas

Area classification	Design value	Attainment date
Moderate (low)***	9.1 up to 12.7 ppm	December 31, 1995
Moderate (high)***	12.8 up to 16.4 ppm	December 31, 1995
Serious	16.5 ppm and above	December 31, 2000

*The primary standard attainment date for ozone is measured from the date of the enactment of the Clean Air Amendments of 1990.

**Severe–15 and severe–17 ozone nonattainment areas have no difference in requirements except for the attainment dates.

***Moderate CO nonattainment areas with design values of 12.7 ppm or less have reduced SIP requirements compared to those areas with design values above 12.7 ppm.

The attainment dates for ozone are in section 181 of the 1990 Clean Air Act Amendments; those for CO are in section 186.

Attainment Status

- Notes show problems with attainment
- Severe and extreme ozone areas not due for attainment until 2005-2010
- Section 185A areas are transitional between attainment and nonattainment
- No serious ozone areas which should have attained by 1999 have done so

Areas Classified as Nonattainment in 1992 that are Nonattainment as of July 1, 2001*

Pollutant	Classification	1992	2001
Ozone	Extreme	1	1
	Severe-17	5	5
	Severe-15	4	4
	Serious	14	14
	Moderate	31	10
	Marginal	42	21
	Section185A	11	4
	Other	2	1
	Incomplete Data	23	15
CO	Moderate<=12.7ppm	32	8
	Moderate>12.7ppm	4	2
	Not Classified	34	11
	Serious	7	7
Lead	N/A	13	4
NO2	N/A	1	0
PM10	Moderate	76	62
	Serious	8	8
SO2	Primary	48	26
	Secondary	6	6

Obtained from data on nonattainment history provided by EPA at <http://www.epa.gov/oar/oagps/greenbk/anay.html>.

*For areas designated as "Not Classified", the number in the final column represents the number of areas that have not yet been designated as attainment areas.

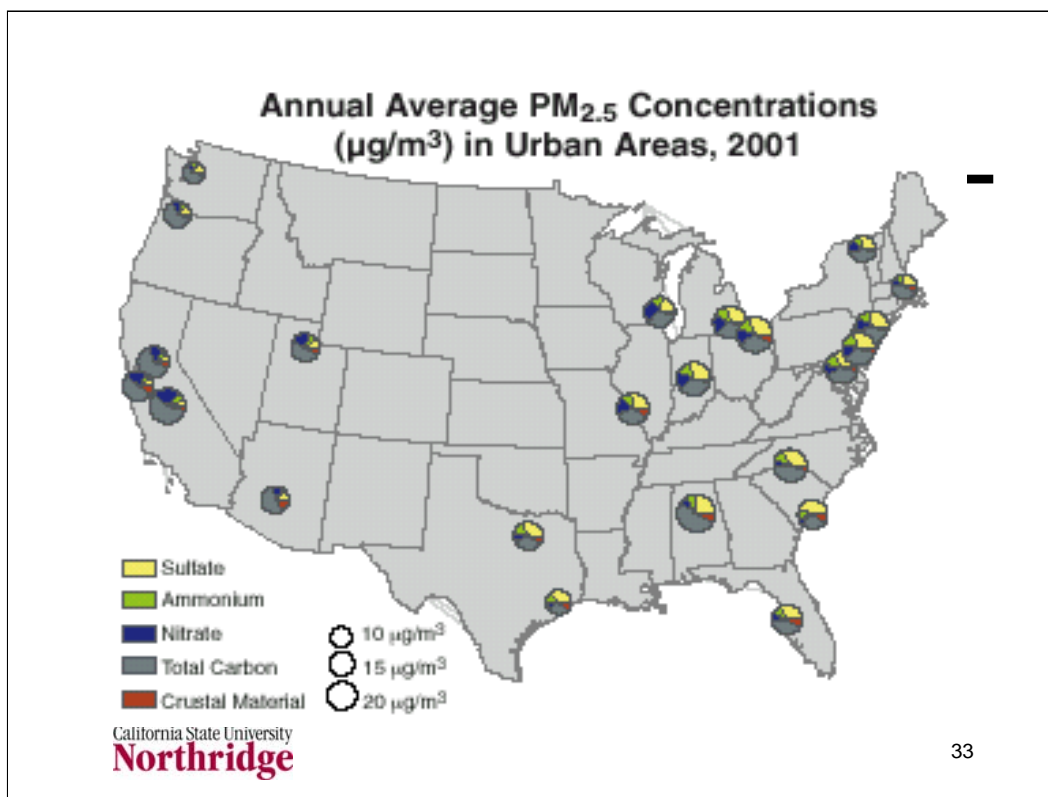
New NAAQS and Visibility

- Eight-hour ozone standard
- Fine particulate (PM_{2.5}) standard
- Promulgated in 1997
- In court until March 2002
- SIPs now being prepared for compliance with new standards
- Regional haze program for 2018 to 2048

The new 8-hour ozone standard is 0.08 parts per million (ppm). This standard applies to the 3-year average of the annual 4th-highest daily maximum 8-hour ozone concentrations. It replaces the old one-hour standard which was 0.12 ppm with a probability that it would not be exceeded more than once a year over a three-year period. EPA set the 8-hour standard at 0.08 ppm because it concluded that there is no discernible threshold below which no adverse health effects occur. Accordingly, no level would eliminate all risk. EPA further concluded that a zero-risk standard was neither possible nor required by the Clean Air Act. They selected the 0.08 ppm level based on their judgment that at this level public health will be protected with an adequate margin of safety. (paraphrased from text at http://www.epa.gov/ttn/oarpg/t1/fact_sheets/o3fact.pdf)

The new PM_{2.5} standards are set at 15 µg/m³, annual arithmetic mean, and 65 µg/m³, 24-hour average. The annual average standard is based on a three-year average of all the “community-based” monitoring stations in an area. The new 24-hour PM standard, the form is based on the 98th percentile of 24-hour PM_{2.5} concentrations in a year (averaged over 3 years), at the population-oriented monitoring site with the highest measured values in an area. (paraphrased from http://www.epa.gov/ttn/oarpg/t1/fact_sheets/pmfact.pdf)

The regional haze program is a separate initiative intended to improve visibility over national parks and monuments known as Class I areas. This is a long-range program in which the first compliance date is 2018 and periodic reviews and improved regulations are scheduled, in ten-year periods, from then to 2048.



This figure is taken from <http://www.epa.gov/airtrends/pm.html>. (Accessed in 2002). It shows the size and species distributions for PM in a variety of regions of the country. A major difference between the eastern and western parts of the US is the larger sulfate concentrations in PM in the east.

With the PM_{2.5} standard, almost none of the fine particulate matter is “crustal” material (i.e., dirt). Much of the PM is carbon coming from carbon particulate and condensed hydrocarbons. Some part of the PM_{2.5} is nitrate. These compositing data imply that methods used to control ozone (VOC and NO_x control) will also have an impact on particulate matter.

Cap-and-Trade Programs

- Emission requirements set for all sources in an area
- Sources have three options
 - Comply with emission limits
 - Produce excess emissions and buy credits from others who generate credits
 - Reduce emissions beyond requirements to generate credits for sale
- Alternative to “command and control”

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Placing a uniform requirement on all existing emission sources is not economically efficient. Some sources may be able to comply easily while others because of their age or other factors may have great difficulty in complying. Cap-and-trade programs are designed to address this efficiency and produce the same environmental benefits at greater cost.

The emissions cap applies to an entire source group in an area. This cap can decrease over time to bring about overall emission reductions.

Environmental concerns about cap-and-trade programs is that they can produce excess emissions in a local area in which a large number of sources choose to purchase credits. Cap-and-trade programs are generally less controversial when they are limited to large sources whose emissions are dispersed over a large area.

Cap-and-trade programs include the Acid Deposition program under the 1990 Clean Air Act Amendments, the RECLAIM program in the South Coast Air Quality Management District for NO_x and SO₂ from large stationary sources, the Northeastern US Ozone Transport region trading program, and the Clean Air Interstate Rule.

Cap-and-trade programs require continuous emission monitors (CEM) with real time reporting of emission results as assurance that each participant in the program is achieving its stated emissions levels.

Reference: National Research Council of the National Academies, *Air Quality Management in the United States*, National Academies Press, 2004, pp 196-209.

Acid Deposition

- Originates with emissions of SO₂ and NO_x
- Reactions in atmosphere form sulfuric and nitric acid from these emissions
- “Acid deposition” is used instead of “acid rain” to account for dry deposition
- Impacts are on ecosystems rather than human health

Acid deposition is an example of a “welfare” benefit as opposed to a human health benefit to be addressed by secondary air quality standards in the Clean Air Act. Because of the overwhelming emphasis on primary standard to protect human health there has been only small attention paid to secondary standards. The problems in ecosystems caused by acid deposition due to SO₂ and NO_x emissions that formed sulfuric and nitric acid in the air had received widespread attention during the 1970s and 1980s, but not much effort was placed into setting standards that would protect these ecosystems.

An extensive study program called the National Acid Precipitation Assessment Program (NAPAP) was started in 1980 and the results of this program inspired the Acid Deposition provisions of the 1990 Clean Air Act Amendments. (Note the title acid deposition as opposed to acid rain acknowledges that nitrate and sulfate particulate matter can deposit on soils and plants causing the same effect as liquid rain with nitric and sulfuric acid.)

One important result of the NAPAP was that sulfuric acid was much more damaging to ecosystems than nitric acid. Thus the initial controls on acid deposition were focused exclusively on SO₂ emissions from power plants.

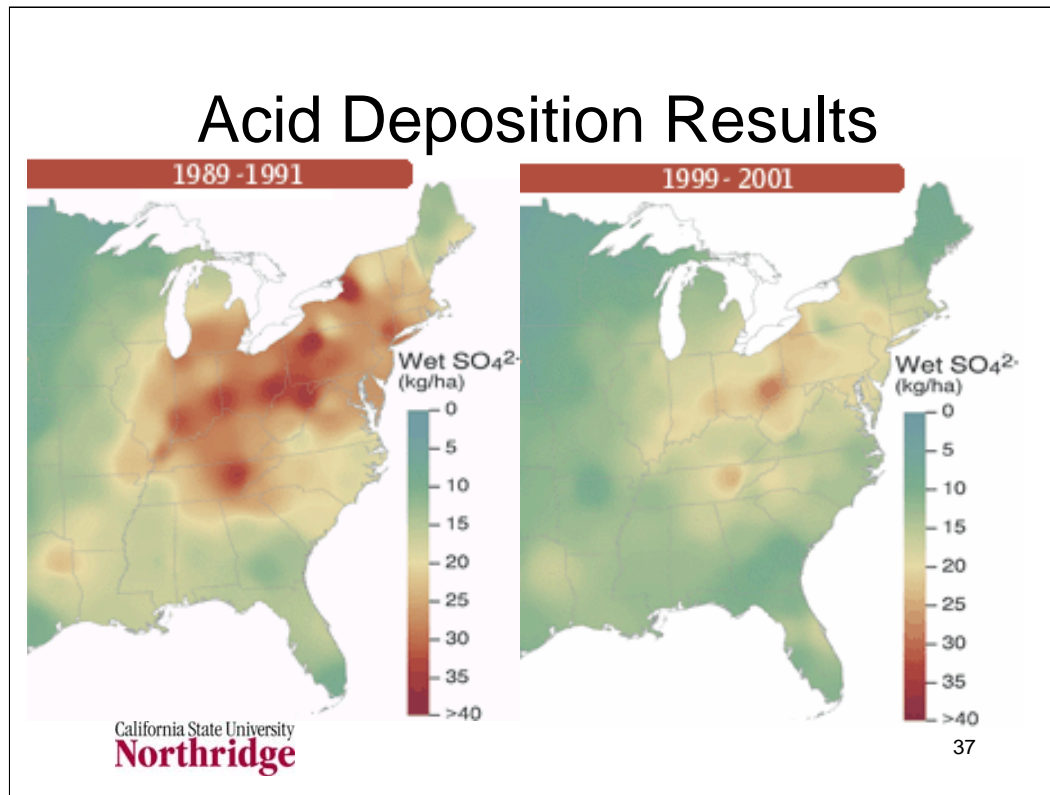
Acid Deposition Controls

- Title IV of 1990 Clean Air Act Amendments
- Market-based, cap-and-trade program
- SO₂ allowances initially assigned to coal-fired power plants
 - Phase I allowances effective 1995
 - Phase II (lower) allowances effective 2000
- NO_x controls also required

In the 1990 Clean Air Act Amendments (1990 CAAA), Congress explicitly set allowances for a set of coal-fired power plants subject to controls. An allowance is the permission to emit one ton per year of SO₂. Allowances were set for 261 specific generating units at 110 different power plants. These levels, effective in 1995, were further reduced in 2000. Plants could bank credits to use after the more stringent requirements became effective. Allowances for the initial stage were set at a rate of 2.6 pounds of SO₂ per million Btu of heat input. For the second stage the allowances were set at 1.2 lb SO₂/MMBtu.

The 1990 CAAA also directed the EPA administrator to set NO_x requirements for NO_x at sources that were subject to SO₂ controls. The specified specific control limits of 0.45 lb/MMBtu and 0.50 lb/MMBtu for different types of coal boilers, levels that could be achieved by using burners designed to produce lower NO_x emissions. More strenuous limits not included in the 1990 CAAA would have required after treatment devices such as selective catalytic reduction (SCR).

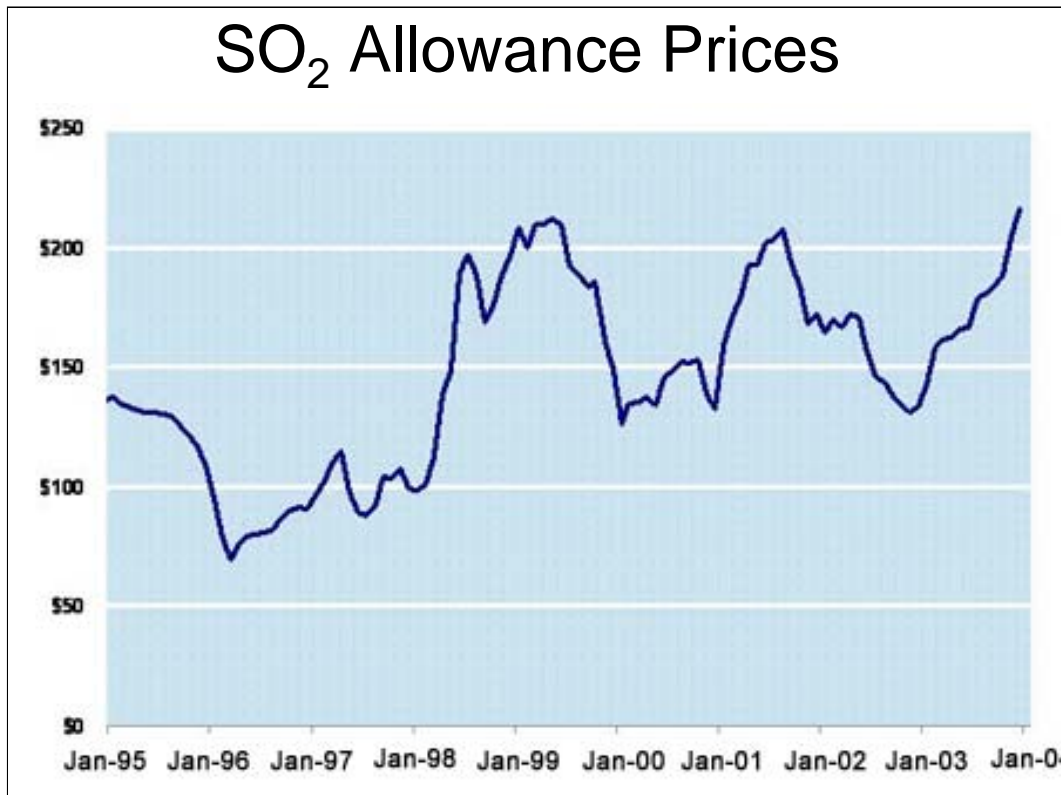
EPA tracks allowances which can be sold by private entities. On a recent day, February 12, 2007, there were 302 allowance transactions listed on <http://cfpub.epa.gov/gdm/index.cfm?fuseaction=allowances.quickreports>



Reference: <http://www.epa.gov/air/clearskies/captrade.html> (accessed February 13, 2007)

These charts show the effectiveness of the acid deposition program with before and after shots of the amount of sulfate ion SO_4^- falling in the northeastern US before immediately before and four to six years after initial implementation of controls under the program. (The units for the deposition are kilograms per hectare. A hectare is 10,000 m^2 which equals 2.471 acres.)

The area shown in this chart was the main area planned to benefit from the acid deposition program. There is a large concentration of coal-fired power plants in this region which came under the acid deposition program.



Reference: <http://www.epa.gov/airmarkets/progress/alprices.html> (Accessed February 13, 2007)

The web site of an allowance trader, <http://www.evomarkets.com/> (accessed February 13, 2007) lists the price for the last transaction on February 13, 2007 as \$500 with a bid and asked price range of \$459 and \$505. The monthly average for January, 2007 was \$455 with a month-end price of \$480.

The acid deposition program is considered a model of the advantages of cap-and-trade programs. Compliance costs have been estimated to be 75% less than originally projected when the program was enacted.

Clean Air Interstate Rule

- Adopted by EPA to meet problems of interstate pollution in Eastern US
 - Required reduction of SO₂ and NO_x
 - Most reductions from power plants
 - Uses cap-and-trade approach administered by EPA
 - States can take alternate approach to meet same emission reduction targets
- Rule vacated (July 11) and reinstated (December 24) in 2008

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Reference: <http://www.epa.gov/interstateairquality/> (accessed February 13, 2007)

This rule was promulgated because of concerns over interstate pollutant transport in the eastern US. The following information was taken from the <http://www.epa.gov/interstateairquality/basic.html> on February 13, 2007.

Under the Clean Air Interstate Rule (CAIR) states are required to meet emission reduction targets. They have two ways of doing this: 1) requiring power plants to participate in an EPA-administered interstate cap and trade system, or 2) develop a set of their own measures.

The Clean Air Interstate Rule (CAIR) provides a Federal framework requiring states to reduce emissions of SO₂ and NO_x. EPA expects states to participate in the cap-and-trade program of the CAIR; it may be necessary for some states to take additional local actions.

If states choose to meet their emissions reductions requirements by controlling power plant emissions through an interstate cap and trade program, EPA's modeling shows that:

In 2010, CAIR will reduce SO₂ emissions by 4.3 million tons -- 45% lower than 2003 levels, across states covered by the rule. By 2015, CAIR will reduce SO₂ emissions by 5.4 million tons, or 57%, from 2003 levels in these states. At full implementation, CAIR will reduce power plant SO₂ emissions in affected states to just 2.5 million tons, 73% below 2003 emissions levels.

continued on next notes page

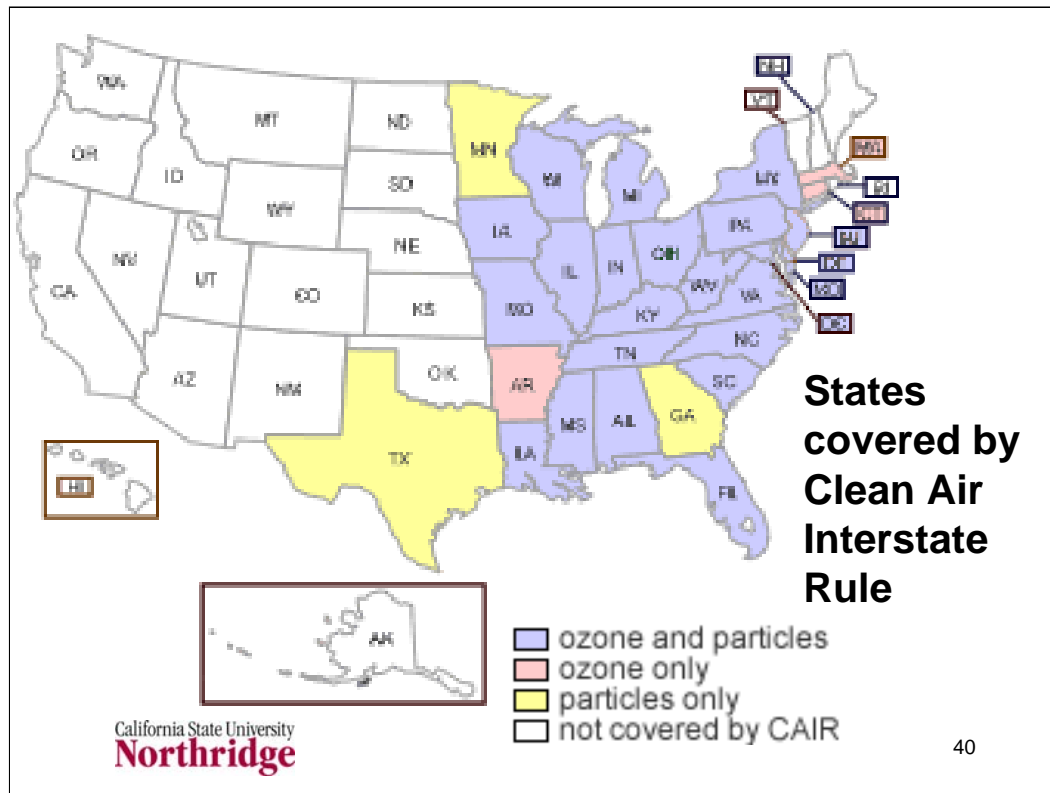


Figure reference: <http://www.epa.gov/CAIR/> (Accessed February 13, 2007)

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CAIR also will achieve significant NO_x reductions across states covered by the rule. In 2009, CAIR will reduce NO_x emissions by 1.7 million tons or 53% from 2003 levels. In 2015, CAIR will reduce power plant NO_x emissions by 2 million tons, achieving a regional emissions level of 1.3 million tons, a 61% reduction from 2003 levels.

In 1990, national SO₂ emissions from power plants were 15.7 million tons compared to 3.5 million tons that will be achieved with CAIR. In 1990, national NO_x emissions from power plants were 6.7 million tons, compared to 2.2 million tons that will be achieved with CAIR.

Permitting Programs

- Operating permits set limits for facility operating conditions and emissions
 - Emissions limits (e.g. pounds per million Btu)
 - Maximum operating rate and hours
- Title V of 1990 CAAA provides national program for operating permits
- Preconstruction review permits
 - New Source Review (NSR)
 - Prevention of Significant Deterioration (PSD)

There are two distinct kinds of permitting programs in air pollution control. The first is the permit to construct. This involves a preconstruction review which is quite elaborate and discussed in detail in the next chart.

The second is the permit to operate. This is a permit that is renewed annually and lists the specific emission limits that a source must achieve for each of its processes.

Prior to the 1990 Clean Air Act Amendments (1990 CAAA) operating permits depended on state law and permit programs had a wide range of stringency. Title V of the 1990 CAAA set up a stringent program for operating permits and gave EPA the responsibility for setting nationwide standards for operating permits.

Large stationary sources are required to have these permits. (Local rules may require permits for smaller sources.) There is a public review process for issuing the permits and once issued, permits are available for public review. Many Title V permits in California can be reviewed starting at the California Air Resources Board web site (accessed February 13, 2007) <http://www.arb.ca.gov/fcaa/tv/tvinfo/permits/permits.htm>

For example the Title V permit for the PG&E compressor station at Hinkley, CA, is <http://www.arb.ca.gov/fcaa/tv/tvinfo/permits/moj/hinkperm.pdf> (accessed February 13, 2007). This permit for a facility that has 44,735 HP of engines (mainly for compressors but also for generators) is 52 pages long.

Preconstruction Review

- Major sources must show compliance with all applicable laws
 - New Source Review in attainment areas
 - Must use emission controls that have Lowest Achievable Emission Rate (LAER)
 - Must offset all emission increases
 - Prevention of Significant Deterioration in attainment areas (PSD)
 - Use best available control technology and keep concentration increase within allowed increment

Reference: <http://www.epa.gov/nsr/> (accessed February 13, 2007)

The term new source review or NSR is sometimes used to refer to all preconstruction review permits for new and modified sources. Major sources as defined by the Clean Air Act or EPA regulations are subject to these requirements. Historically, the term New Source Review was applied to reviews of new sources in nonattainment areas and reviews of new sources in nonattainment areas were referred to as PSD permits.

According to the review of air quality management in the US done by a committee of the National Research Council, NSR has had significant impact on reducing emissions. However, the requirements for NSR have become so complex that it is difficult to understand them all.

One indication of this is that the EPA manual for constructing such reviews is still called a draft manual even though it was first published in 1990.

Many proposals for reforming NSR have been considered over the past 20 years. No major changes were formally proposed by EPA until the Bush administration made several revisions to the NSR regulations. Some of these have been controversial and some have been taken to court as not being consistent with the original legislative intent for provisions in the Clean Air Act.

Clear Skies Initiative

- Proposed by White House/USEPA
- Applies to electric power plants
- Controls SO₂, NO_x and mercury
- Implementation schedule until 2018
- Would replace NSR for power plants
- EPA report shows benefits
- Has lacked congressional support in past and other rules are in place

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Reference: <http://www.epa.gov/air/clearskies/basic.html> (accessed February 13, 2007)

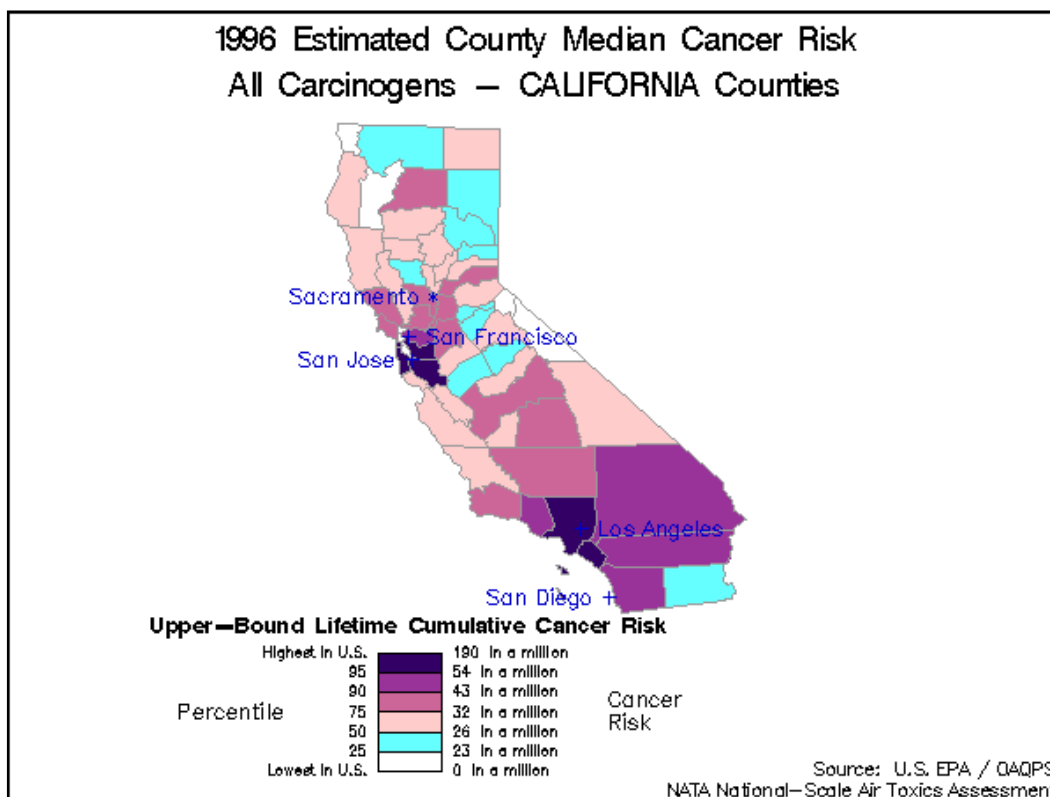
This is (was) an ambitious plan to have a coordinated control package for electric power plants. Emissions of SO₂, NO_x, particulate matter and mercury would be controlled in a coordinated multipollutant approach. All controls would be under a cap-and-trade system.

The proposed program received significant criticism for (1) not addressing CO₂ emissions at the same time as it was considering a comprehensive multipollutant approach and (2) environmental critics did not like the very long compliance schedule.

Although the plan is still claimed to be a better alternative to other approaches for controlling pollution from electric power plants, it has not been actively pushed by the White House or the EPA. Congressional opposition to the plan, which was significant before the 2006 elections is likely to be even greater now and the plan will almost certainly not pass in its present form.

Despite opposition to the plan as originally and currently proposed, the kind of approach proposed here – a cap-and-trade program, with a multipollutant approach is generally regarded as a more efficient approach to air pollution control.

A power point presentation on the proposed emission limits under this program is available at http://www.epa.gov/air/clearskies/clearskies_hotspots.pdf (accessed February 13, 2007)



Reference: map generated starting from <http://www.epa.gov/ttn/atw/nata/maprisk.html> on February 13, 2007. The text below is taken from the “intended use” link on the map page.

The results of the national-scale assessment will provide important information to help EPA continue to develop and implement various aspects of the national air toxics program. They will not be used directly to regulate sources of air toxics emissions. While regulatory priority setting will be informed by this and future national assessments, risk-based regulations will be based on more refined and source-specific data and assessment tools. More specifically, the assessment results will help to:

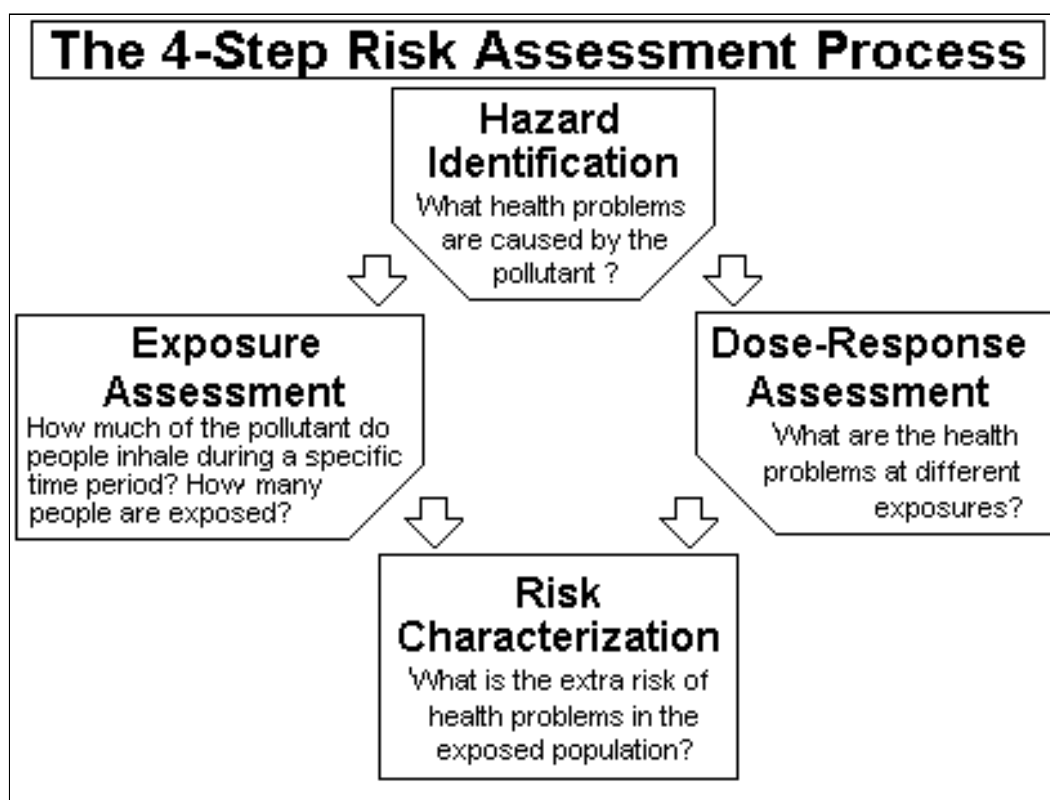
Identify air toxics of greatest potential concern.

Characterize the relative contributions to air toxics concentrations and population exposures of different types of air toxics emissions sources (e.g., major, mobile).

Set priorities for the collection of additional air toxics data and research to improve estimates of air toxics concentrations and their potential public health impacts. Important additional data collection activities will include upgraded emission inventory information, ambient air toxics monitoring, and information on adverse effects to health and the environment.

Establish a baseline for tracking trends over time in modeled ambient concentrations of air toxics.

Establish a baseline for measuring progress toward meeting goals for inhalation risk reduction from ambient air toxics.



Reference: http://www.epa.gov/ttn/atw/3_90_024.html (Accessed February 13, 2007)

The **hazard identification** process considers specific effects attributed to the pollutant as well as the weight of evidence for the problems. A variety of health problems are considered, but cancer is the most common concern when considering toxic air contaminants.

Exposure assessment is done by models that consider the diffusion and mixing of pollutants in the air after the exposure from their source until they reach populations that breathe the pollutants.

Dose-response assessment considers how pollutants can enter the body. Although inhalation is the primary route for air toxics, some air toxics may fall to the ground or be taken up by animals and later ingested as food. Another important question about dose-response relationships is the question of whether or not there is a threshold concentration below which there are no effects. Carcinogens (cancer causing chemicals) are usually presumed to have no threshold.

Risk characterization considers how the assessment of the response of an individual to specific concentrations is matched by the concentrations that a population would encounter in the environment.

Power Plant Mercury

- Considered separately from other toxic pollutants in 1990 CAAA
 - Required EPA to study issue and report to congress
 - Completed report recommended controls over mercury from power plants
- Clean air mercury rule issued May 2005 creates cap-and-trade program for power plant mercury

Reference: <http://www.epa.gov/mercury/> (accessed February 13, 2007)

The report to congress noted that the main route by which mercury emissions entered humans was through eating fish that accumulated mercury. However, the report also noted that there were large uncertainties in the source of mercury in fish, some, if not most, of which could come from other sources. Although the report led to a finding that regulation of mercury was “necessary and appropriate” in 2000, EPA recently reversed this finding because of the uncertainties in the mercury study. Despite this reversal they still passed the clean air mercury rule.

This rule sets new source performance standards (NSPS) for mercury emissions from power plants and contains a cap-and-trade rule for mercury emissions. Under this rule the 1999 level of mercury emissions (48 tons) will be reduced to 38 tons in 2010 and 15 tons in 2018.

Climate Issues

- Planetary energy balance
 - Greenhouse effect
 - Stratospheric ozone
- Provide introduction now, cover later
- Stratospheric ozone has general agreement
- Most recent IPCC report on global warming very certain about effect

The planetary energy balance between incoming solar radiation and outgoing infrared radiation is affected by two main sources. The first is the ozone layer in the stratosphere. This layer is formed by photochemical reactions that can be disturbed by human emissions that reach there.

The intergovernmental panel on climate change (IPCC) is a UN organization that examines scientific opinion on climate change. They prepare a report every six years. See <http://www.ipcc.ch/> (accessed February 13, 2007) A new report is scheduled for release later this year. A brief report, called a summary for decision makers, was released in early February.

“the balance of evidence suggests that there is a discernible human influence on global climate,” the Third Assessment Report states the influence of human activities on climate in even starker terms. It concludes that, “[I]n light of new evidence and taking into account the remaining uncertainties, most of the observed warming over the last 50 years is likely to have been due to the increase in greenhouse gas concentrations” (IPCC 2001).

“Warming of the climate system is unequivocal, as is now evident from observations of increases in global average air and ocean temperatures, widespread melting of snow and ice, and rising global average sea level.”(IPCC 2007)

Stratospheric Ozone

- Ground level (tropospheric) ozone is a pollutant
- Stratospheric ozone reduces UV radiation reaching planet's surface
- Cl atoms that reach the stratosphere can destroy ozone there
- Chlorofluorocarbons (CFCs) good for ground-level, bad for stratosphere

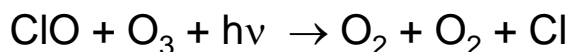
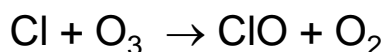
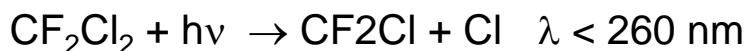
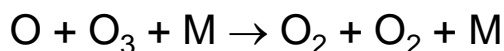
Although ground level ozone has deleterious effects on human health, ozone in the stratosphere acts to reduce incoming solar radiation. Without this ozone the planetary energy balance would be different and the amount of high energy ultraviolet radiation would add to the intensity of the current solar radiation.

Ozone in the stratosphere has a natural cycle that is disturbed by chemicals produced from human activities. The major problem is with a class of compounds known as chlorofluorocarbons, which consist of chlorine, fluorine, and carbon atoms. These compounds are very inert and have been used as refrigerants since the 1920s. They have also found application as solvents. For several years they were a preferred alternative to traditional solvents because they did not react to form ozone in the troposphere.

However, because of their stability they migrated to the stratosphere where they interfered with the natural ozone cycle, removing ozone from the stratosphere. (See the chemical mechanism on the next page.)

Nitric oxide can also interfere with ozone in the stratosphere. When the idea of supersonic passenger travel was considered there was a concern that NO_x emissions from SSTs flying in the stratosphere could also interfere with ozone. Fortunately for the ozone layer, SSTs did not prove an economic alternative for passenger travel.

Stratospheric Photochemistry



The first two reactions provide for the production of ozone; the second two for the destruction of ozone. These four reactions lead to a natural equilibrium concentration of ozone in the stratosphere.

The ozone concentration peaks in a region between 20 and 30 km above the earth's surface and the concentration there is over ten times that at the earth's surface.

CFC's that reach the stratosphere can be photolyzed releasing Cl atoms. These atoms can react with ozone creating a new equilibrium that reduces the normal ozone concentration by as much as 60% in arctic regions (the so-called ozone hole.)

The Montreal protocol of 1987 as revised in 1992 calls for the complete elimination of CFCs by the beginning of 1996 in developed countries. New HFC refrigerants like R-134a have replaced older CFC refrigerants like R-11 and R-22.

Greenhouse Gases

- Incoming solar radiation mainly in UV and visible
- Outgoing terrestrial radiation infrared
- Atmospheric gases absorb different amounts at different wavelengths
- Greenhouse gases: CO₂, CH₄, N₂O
- Equivalent tons of carbon measure

The impact of greenhouse gases has been hypothesized for many years. In particular, anthropogenic emissions of CO₂ have increased ambient CO₂ levels and continued CO₂ emissions are forecast in the future. Since CO₂ is a strong absorber of IR radiation, it will reduce the energy leaving the earth's surface as it increases.

The main concern over greenhouse gases is the uncertainty about the ultimate impact. There are many interactions to consider. For example a warmer climate will allow more water vapor in the air. This may lead to the formation of more clouds. The additional clouds will scatter more incoming radiation and absorb (and scatter) outgoing radiation.

The recent report by the United Nations Intergovernmental Panel on Climate Change predicted an increase in the global average temperature between 1.1°C and 6.4°C depending on the future emissions (possible changes in national policies to reduce greenhouse gases) as well as the uncertainty for each emission scenario.

Reference: <http://www.ipcc.ch/SPM2feb07.pdf> (accessed February 8, 2007).